



(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
15.12.1999 Bulletin 1999/50

(21) Application number: 98961455.7

(22) Date of filing: 21.12.1998

(51) Int. Cl.⁶: **D01C 3/00**, **D01B 7/00**

(86) International application number:
PCT/JP98/05784

(87) International publication number:
WO 99/34038 (08.07.1999 Gazette 1999/27)

(84) Designated Contracting States:
DE FR GB IT

(30) Priority: 25.12.1997 JP 36739597

(71) Applicants:
• JAPAN as repr. by DIR. GENERAL of NATIONAL
INST. OF SERICULTURAL & ENTOMOLOGICAL
SCIENCE MINISTRY OF AGR, FORESTRY &
FISHERIES
Tsukuba-shi Ibaraki-ken 305-8634 (JP)
• EAUDELEMAN Co., Ltd.
Osaka-shi, Osaka 553-0003 (JP)

• Tsubouchi, Kozo
Kitasouma-gun, Ibaraki 302-0102 (JP)

(72) Inventors:
• TSUBOUCHI, Kozo
Kitasouma-gun, Ibaraki 302-0102 (JP)
• FUJIURA, Shoko,
Eaudeleman Co., Ltd.
Osaka-shi, Osaka 553-0003 (JP)

(74) Representative:
Goddard, Heinz J., Dr.
FORRESTER & BOEHMERT
Franz-Joseph-Strasse 38
80801 München (DE)

(54) **MODIFIED SILK MATERIALS AND PROCESS FOR THE PRODUCTION THEREOF**

(57) Objects of the present invention is to widen an applicability of carbonized silk utilizing improved properties thereof, to provide an incompletely carbonized product or denatured silk useful for various purposes because of both inherent and carbonized properties thereof by heat-treating silk as a raw material under a mild condition so as to control an extent of carbonization, and to provide an industrially practical method for preparing a denatured silk material by controlling a cost of energy consumption due to heat treatment.

There is provided a method for preparing a denatured silk material of various colors by heat-treating natural silk, half-degummed silk or degummed silk or a mixture thereof in an atmosphere of air flow under 0.5 to 1.5 atmospheres at a temperature of 150 to 500 °C for a certain period of time.

Description

TECHNICAL FIELD

- 5 [0001] The present invention relates to a variously useful denatured silk material obtained by heat-treating silk in a gas flow.
- [0002] The silk material of the present invention can be used for a purpose as a raw material of an outer skin coating product for human use such as outer skin preparations, non-medical skin agents and beauty products or as a medical material, for a purpose as a plant growth promoter, or for other purposes such as an absorbent, a filter material and an
- 10 abrasive material.

BACKGROUND TECHNOLOGY

- [0003] A raw material of outer skin coating products such as an eyebrow pencil and a hair dye has conventionally
- 15 prepared by heat treatment of organic materials and, in particular, by incomplete combustion of petroleum materials.
- [0004] Carbonized materials obtained by heat treatment of plants are used as an absorbent and a filter material.
- [0005] However, those materials prepared by incomplete combustion of petroleum are apt to generate carcinogenic substances or contaminated therewith during their heat treatment, and therefore are forbidden to use, for example, in the United States.
- 20 [0006] An example of such a material other than petroleum products is described in JP-A No. 8-59,219 in which silk is subjected to heat treatment to prepare a carbonized product useful as an outer skin coating product or a filter material.
- [0007] The above mentioned heat treatment of silk is conducted in an inert gas atmosphere at a temperature of 600 to 2,000 °C.
- 25 [0008] The heat treatment temperature of 600 °C or higher is selected to accomplish carbonization.
- [0009] At the heat treatment temperature below 600 °C a carcinogenic substance (such as benzopyrene) would be formed, while silk as a raw material is changed to a state of tar due to wax, etc. contained therein, which provides a carbonized product without yielding fine particle or granular products sufficiently useful for practical use.
- [0010] There is also described that the heat treatment temperature is limited up to 2,000 °C from a viewpoint of industrial cost-performance so as not to increase energy consumption at higher temperatures. According to the conventional invention, however, the raw material is excessively carbonized by the heat treatment so that a range of application thereof is limited to an extreme.
- 30 [0011] The present invention is achieved in the technical background as described above.
- [0012] Accordingly, it is an object of the present invention to widen an applicability of carbonized silk utilizing improved properties thereof.
- 35 [0013] Another object of the present invention is to provide an incompletely carbonized product (or denatured silk) useful for various purposes because of both inherent and carbonized properties thereof by heat-treating silk as a raw material under a mild condition so as to control an extent of carbonization.
- [0014] Still another object of the present invention is to provide an industrially practical method for preparing a denatured silk material by controlling a cost of energy consumption due to heat treatment.
- 40

DISCLOSURE OF THE INVENTION

- 45 [0015] As a result of the inventors' experiments on conditions of silk heat treatment, it was found that an extent of carbonization of a raw silk material to be heat-treated can be variously controlled, while a cost of energy consumption due to the heat treatment is reduced enough to conduct the present method industrially.
- [0016] The present invention is achieved on the basis of the above mentioned information and, as will be described in the following, provides a method for preparing a denatured silk material by heat-treating silk under a specific condition, and a denatured silk material used for purposes as an outer skin coating product for human body, a medical material, a plant growth promoter, an absorbent, a filter material and an abrasive material.
- 50 [0017] Namely, according to the present invention, it is provided (1) a method of preparing a denatured silk material of various colors by heat-treating natural silk, half-degummed silk or degummed silk or a mixture thereof in an atmosphere of air flow under 0.5 to 1.5 atmospheres at a temperature of 150 to 500 °C for a certain period of time.
- [0018] It is also provided (2) a method of preparing a denatured silk material described in the above item (1) wherein
- 55 a heat-treatment period is in a range of several minutes to 20 hours.
- [0019] It is also provided (3) a method of preparing a denatured silk material of various colors by heat-treating natural silk, half-degummed silk or degummed silk or a mixture thereof in an atmosphere of inert gas flow selected independently from nitrogen, helium, neon, argon, krypton and xenon or mixture thereof under 0.5 to 1.5 atmospheres at a tem-

perature of 150 to 500 °C for a certain period of time.

[0020] It is also provided (4) a method of preparing a denatured silk material described in the above item (3) wherein the heat-treatment period is in a range of several minutes to 20 hours.

[0021] It is also provided (5) a method of preparing a denatured silk material described in any of the above item (1) or (4) wherein natural silk, half-degummed silk, degummed silk or a mixture thereof is in the form of a film, powder, fiber, yarn, fabric, braid or mixture thereof.

[0022] It is also provided (6) a method of preparing a denatured silk material described in any of the above item (3) or (4) wherein various colors include black, yellow, brown, dark brown, red, purple, blue and gray or natural tints thereof.

[0023] It is also provided (7) a denatured silk material of various colors by heat-treating natural silk, half-degummed silk or degummed silk or a mixture thereof in an atmosphere of air flow under 0.5 to 1.5 atmospheres at a temperature of 150 to 500 °C for a certain period of time.

[0024] It is also provided (8) a denatured silk material described in the above item (7) wherein a heat-treatment period is in a range of several minutes to 20 hours.

[0025] It is also provided (9) a denatured silk material of various color by heat-treating natural silk, half-degummed silk or degummed silk or a mixture thereof in an atmosphere of inert gas flow selected independently from nitrogen, helium, neon, argon, krypton and xenon or mixture thereof under 0.5 to 1.5 atmospheres at a temperature of 150 to 500 °C for a certain period of time.

[0026] It is also provided (10) a denatured silk material described in the above item (9) wherein the heat-treatment period is in a range of several minutes to 20 hours.

[0027] It is also provided (11) a denatured silk material described in any of the above item (7) to (10) wherein the material is used for a purpose as an outer skin coating product for human use.

[0028] It is also provided (12) a denatured silk material described in the above item (11) wherein the outer skin coating product for human use is a medical material for outer skin, non-medical material for outer skin or beauty products.

[0029] It is also provided (13) a denatured silk material described in any of the above item (7) to (10) wherein the denatured silk material is used for a purpose as a medical material.

[0030] It is also provided (14) a denatured silk material described in any of the above item (7) to (10) wherein the denatured silk material is used for a purpose as a plant growth promoter.

[0031] It is also provided (15) a denatured silk material described in any of the above item (7) to (10) wherein the denatured silk material is used for a purpose as an absorbent or a filter material.

[0032] It is also provided (16) a denatured silk material described in any of the above item (7) to (10) wherein the denatured silk material is used for a purpose as an abrasive material.

[0033] A starting material of denatured silk material of the present invention includes natural silk, half-degummed silk, degummed silk or a mixture thereof.

[0034] The silk material is in the form of a powder, fiber, yarn, (such as knitted goods, woven and nonwoven fabrics,) braiding, or a mixture thereof.

[0035] As a rule, silk is a generic term including cocoon yarn, raw silk, and silk thread and, for example, cocoon yarn comprises protein containing about 28 % of sericin which wraps up fibroin.

[0036] The term "degummed silk" used herein means those materials which are treated with hot water containing soap, surfactants such as an enzyme activator, or alkaline substances such as sodium carbonate, sodium silicate, etc. (so-called "alkaline degumming"), treated with warm water containing enzymes such as chymotrypsin, alkalase, papain, etc. (so-called "enzyme degumming"), and biologically treated with microorganisms (so-called "biological degumming") to remove sericin along with wax and inorganic substances.

[0037] The term "natural silk" used herein means those materials which are not degummed.

[0038] The term "half-degummed silk" means intermediate materials between degummed and natural silk which generally contain less than 15 % of sericin.

[0039] According to the present invention, such a heat treatment is conducted at a temperature in the range of 150 to 500 °C.

[0040] The reason why is that silk is completely carbonized or burned at a temperature more than 500 °C within several minutes in the case of air flow treatment, while an extent of carbonization is hard to control when silk is treated in an inert gas flow such as nitrogen, helium, etc.

[0041] Further, it takes an impracticably long period of time to carbonize silk at a temperature less than 150 °C either in the air or inert gas flow.

[0042] As the heat treatment of the present invention is conducted at such a rather lower temperature range, a cost of energy consumption can be reduced with great industrial advantage.

[0043] In addition, as the heat treatment of the present invention is conducted in a gas flow under 0.5 to 1.5 atmospheres (1 atm. = 1,013 Hp), volatile components caused by heat decomposition of silk are removed out of the reaction system by the gas flow without forming tar-like products as described in JP-A 8-59,219.

[0044] That is to say, the heat treatment can be conducted without residual impurities in a denatured silk material.

[0045] As a result, the denatured silk material thus heat-treated is dry enough to yield fine particle or granular products with ease.

[0046] The starting silk material can be heated stably and effectively in the range of atmosphere described above.

[0047] The denatured silk materials of fine particle or granular form is easily obtained by mechanically grinding the starting silk material in the form of film or fabric because tensile strength thereof is extremely decreased by the heat treatment.

[0048] The denatured silk material of the present invention changes colors thereof starting from white to pale yellow, yellow, brown, olive brown, blue, purple, brownish black and finally to black in order depending on an extent of the heat treatment. Accordingly, the denatured silk material in a powdery state, for example, is used as a basic material of outer skin coating products for human use such as foundation cream, an eyebrow pencil, hair dye, cheek rouge, manicure, lipstick, eye shadow, etc.

[0049] In this case, the heat treatment may be quickly terminated when a desired color appears, which provides the denatured silk material of various colors.

[0050] Because, the heat treatment can be easily terminated at a temperature of 500 °C or less in the heating atmosphere.

[0051] The denatured silk material thus prepared assumes various colors depending on an amount of uncarbonized (silk) residue, which varies due to the extent of carbonization, and also partially possesses a biocompatible function intrinsic to silk.

[0052] Thus, the denatured silk material of the present invention positively exhibits both properties of carbonized substance and silk itself, which makes it possible to widen an applicability thereof for various purposes.

[0053] For example, the present silk material may be used not only for purposes as a medical material and outer skin coating products for human use which are direct in contact with skins but also for purposes as a plant growth promoter, absorbent, filter material, abrasive material, etc.

[0054] The utility for these purposes is evident from examples 6 to 11, described later.

[0055] As has been described above, the starting silk material of the present invention may be in the form of a film, powder, fiber, yarn, fabric (such as knitted goods, woven and nonwoven fabrics), braiding or mixture thereof.

[0056] When the starting material is kept in the original form after the heat treatment, the denatured silk material may be used as it is.

[0057] For example, when starting silk fabrics (such as knitted goods, woven or nonwoven fabrics) is heat-treated, the thus formed product is quite suitable as a material of improved absorbing properties, because such a product has a larger surface area per unit volume due to characteristic three-dimensional twist structure of fabric fibers.

[0058] On the other hand, the denatured silk material of the present invention may be mechanically ground to form a powder having particle size of 0.01 to 10 micron.

[0059] The denature silk material having particle size less than 0.01 micron is costly to produce and, in addition, not necessarily fine for practical use.

[0060] Particles of 10 micron or more are generally hard to aggregate because of larger particle size so that the denature silk material does not sufficiently get to fit skins than expected or exhibits a sense of incompatibility toward skins for certain purposes thereof to be use.

[0061] When the denature silk material of the present invention is used as a filter material, however, preferable particle size is 0.01 to 20 mm.

[0062] According to the present invention, there is provided a denature silk material useful for various purposes because of both inherent and carbonized properties thereof by heat-treating silk as a raw material under a mild condition, i.e., in a gas flow of 0.5 to 1.5 atmospheres at a temperature of 150 to 500 °C so as to control an extent of carbonization.

[0063] Further, although a condition of relatively lower temperature is employed in the present invention, the heat treatment in a gas flow under 0.5 to 1.5 atmospheres allows to remove volatile components caused by heat decomposition of silk out of the reaction system by the gas flow without forming conventional tar-like products.

[0064] Furthermore, as the heat treatment of the present invention is conducted at such a relatively lower temperature range, a cost of energy consumption can be reduced, thereby providing a method of fabricating with great industrial advantage.

BEST MODE FOR CARRYING OUT THE INVENTION

[0065] The present invention will be further detailed by the following examples, however, these examples are not to be constructed to limit the scope, and variations may be made without departing from the spirit and scope of the present invention.

[0066] For example, waste of silk products may also be used as the starting material.

Example 1

[Preparation of denature silk material of various colors]

5 [0067] Five grams of crystalline silk powder (similar one as described in Japanese Registered Patent No. 2,615,440) was charged in a horizontal glass tube, which was then horizontally placed in an electric furnace, [available from Shinyo Rikagaku Kizai Co., Ltd as Model KP-7] to subject the crystalline silk powder to a heat treatment by heating from room temperature at a heating rate of 10 °C / min. while flowing nitrogen gas from one end of the glass tube to the other so as to keep a gas pressure of 1 ± 0.1 atm.

10 [0068] Change in colors of the crystalline silk in the process of heating was visually observed.

[0069] A similar procedure was carried out using argon gas, and a visual observation was repeated as the same manner as described above.

[0070] A result thus obtained is shown in the attached Table 1.

Table 1

temperature °C	color	
	nitrogen gas	argon gas
25	white	white
100	white	white
150	white	white
200	white	white
220	pale yellow	pale yellow
240	pale yellow	pale pink
250	yellow	flesh pink
260	brown	skin color
270	brown	pale reddish brown
280	dark brown	blackish brown
290	blackish brown	blackish brown
300	blackish brown	dark blackish brown
310	black	black
320	black	black
330	black	black

[0071] No difference in colors was observed between nitrogen and argon within a substantial temperature except that the color changed to slightly red in the range of 240 to 280 °C in the argon atmosphere.

Example 2

[Preparation of dark brown particles of 5 micron]

50 [0072] Raw silk was soaked in a 0.1 %-aqueous solution of sodium carbonate having a bath ratio of 1 : 50, boiled therein for one hour followed by further boiling in renewed aqueous sodium carbonate for additional one hour, washed with water and dried to yield silk yarn (fibroin fiber).

[0073] When the degummed silk yarn was then burned by heating using the apparatus in the example 1, i. e., in the electric furnace at 280 °C in an argon atmosphere at a gas pressure of about 0.5 atm. for 3 minutes, the silk yarn was partially carbonized to yield a reddish dark brown burned product or denatured silk material which partially exhibited properties of silk protein.

[0074] The thus denatured silk material was ground by means of a microjet grinder [available from Hosokawa Micron Co., Ltd.] followed by classification to yield particles having particle size of about 5 micron.

Example 3

[Preparation of fabric-like denatured silk material]

5 [0075] Five grams of silk fabric was charged in a horizontal glass tube, which was then horizontally placed in an electric furnace, [available from Shinyo Rikagaku Kizai Co., Ltd. as Model KP-7], to subject the silk fabric to a heat treatment by heating from room temperature at a heating rate of 10 °C / min. while flowing air from one end of the glass tube to the other so as to keep a gas pressure of 1 ± 0.1 atm.

[0076] Change in colors of the silk fabric in the process of heating was visually observed.

10 [0077] Results obtained were shown in the attached Tables 2 to 4.

Table 2

under an airflow of 1 atm. at a predetermined temperature of 170 °C			
time period	1~2 hours	2~5 hours	10~20 hours
color of silk fabric	pale yellow	yellow	brown

Table 3

under an air flow of 1 atm. at a predetermined temperature of 250 °C						
time period	0.3 ~ 2 minutes	8 ~ 20 minutes	0.5 ~ 1 hour	0.5 ~ 3 hours	4 ~ 6 hours	more than 7 hours
color of silk fabric	pale yellow	brown	reddish dark brown	purply brown	blackish brown	black

Table 4

under an air flow of 1 atm. at a predetermined temperature of 320 °C					
time period	20 ~ 40 seconds	1 ~ 2 minutes	2.5 ~ 4 minutes	5 ~ 10 minutes	more than 13 minutes
color of silk fabric	brown	reddish dark brown	pale dark brown	dark brown	black

45 [0078] The thus heat-treated silk fabric, especially those materials which were colored brown or darker colors than reddish dark brown, can be mechanically ground with ease, for example, by means a microjet grinder to yield colored silk powders.

Example 4

[Variation in pressure]

[0079] In order to yield denatured silk materials under a different burning condition, a similar experiment was carried out in a similar manner as described in Example 1 except applying the pressure of 1.6 atm.

55 [0080] Further, Example 1 was repeated under a condition of 0.4 atm. As a result, it was found that stable rise in temperature of the crystalline silk powder can not be achieved in the glass tube.

Example 5

[Preparation of purple and blue powder]

5 [0081] Yamamai silk yarn was soaked in a 0.1 % sodium carbonate aqueous solution having a bath ratio of 50 for one hour, washed with water and dried to yield degummed silk yarn as a material to be heat-treated.

[0082] The thus degummed silk yarn was burned in an atmosphere of 240 °C (burning time for 10 minutes) by means of the same apparatus used in the [Example 1] to yield a predominantly purple- and blue-colored mixture of denatured silk material as a burned product.

10

Example 6

[Application as an outer skin coating product]

15 [0083] White (at treating temperature of 25 °C), pale yellow (at treating temperature of, 220 °C) and blackish brown (at treating temperature 300 °C) denatured silk materials obtained by the heat treatment of [Example 1] were mixed with a beauty product for skin care to prepare four test samples A, B, C and D comprising different components as in the following.

[0084] About 0.05 g of these samples A to D were applied to hypersensitive back skins (of allergic subjects) on the area of 3 cm x 3 cm for 24 hours (as an open batch test).

20

[0085] As a result, the sample A as a control caused slight itchiness after application thereof.

[0086] On the other hand, samples B, C and D made the applied skin more smooth than that of an unapplied portion without causing itchiness.

[0087] Especially in the case of the sample B, the skin was comfortably wet and quite smooth with no itchiness.

25

A : a general beauty product (containing talc, kaolin and zinc oxide as a main component).

B : 100 % of the (white) silk material.

C : 50 % of the control sample A and 50 % of the (pale yellow) denatured silk material.

D : 50 % of the control sample and 50 % of the (blackish brown) denatured silk material.

30

Example 7

[Application as a plant growth promoter]

35 [0088] Ten grams of brown denatured silk material obtained by the heat treatment of [Example 1] (at a treating temperature of 260 °C) was added to 1,000 g of water.

[0089] The thus prepared mixture of the denatured silk material and water (in an amount of 100 g) was applied once a week to seedlings of a Madagascar periwinkle planted in a planter of about 20 cm wide, about 60 cm long and about 15 cm high.

40

[0090] After two months, a plant growth promoting effect of the denatured silk material was observed.

[0091] A treated group of Madagascar periwinkles (in bundles of ten plants) and an untreated control group of Madagascar periwinkles (in bundles of ten plants), were cut down above the ground and weighed. It was found that weight of the untreated bundle of Madagascar periwinkles was 110 g, while that of the treated bundle of Madagascar periwinkles was 150 g.

45

Example 8

[Application as an absorbent]

50 [0092] Two grams of dark brown crystalline silk powder obtained by the heat treatment of [Example 3] (see, Table 4) was put in a cotton bag, which was kept for 5 hours in one liter of slightly muddy fresh water (collected from Lake Biwa). As a result, transparency of the water was improved with little muddiness.

Example 9

55

[Application as an odor absorbent (deodorant)]

[0093] A whole body of rotten fish (of 300 g in weight) was left in a sealed chamber of about 6 m³ for one hour and,

after the fish taken out of the chamber, 100 g of the dark brown crystalline silk powder obtained by the heat treatment of [Example 3] (see, Table 4) was used to keep therein.

[0094] After 6 hours, odor of the rotted fish was decreased to a relatively low level.

5 Example 10

[Application as an abrasive material]

[0095] The white (at treatment temperature of 100°C) and brown (at treatment temperature of 270°C) crystalline silk powders obtained by the heat treatment of [Example 1] were used as an abrasive material.

[0096] Glass and metal (copper) plates as test specimens were wiped thoroughly with an alcohol containing glass polish cloth and subjected to an abrasion process by putting the white silk powder on the surface of each specimen in an amount of 2 g / 50 cm² and polishing with a dry glass polish cloth and then a plastic board under pressure of 10 kg / cm² for one hour.

[0097] Further, the glass and metal surfaces were thoroughly polished with the alcohol containing glass polish cloth. As a result of visual observation of the glass and metal surfaces by a reflecting test, it was found that brilliance of the specimens was improved due to the abrading process.

[0098] The reddish brown crystalline silk powder obtained by the heat treatment of [Example 3] (see, Table 3) was used for an abrading test in a similar manner as described above.

[0099] As a result of visual observation of the glass and metal surfaces by a reflecting test, it was found that brilliance of the specimens was improved to an extent slightly higher than that of the white crystalline silk powder.

Example 11

[Application as a filter (a filter material)]

[0100] The white crystalline silk powder obtained by the heat treatment of Example 1 at a treating temperature of 100 °C (see, Table 1) was used to test as a filter material.

[0101] The white silk powder was put between two flat boards and pressed under pressure of 20 kg / cm² to harden, thereby yielding a powder board of 2 mm in thick.

[0102] The powder board was sandwiched between filter paper to form a filter material. Water collected from Lake Biwa was filtered under 0.5 atm. by means suction using the thus prepared filter material, thereby yielding water of considerably improved muddiness.

[0103] The reddish brown crystalline silk powder obtained by the heat treatment of [Example 3] (see, Table 3) was used for a filtering test in a similar manner as described above.

[0104] As a result, it was found that muddiness of the filtrate was considerably improved to an extent lower than that of the white crystalline silk powder.

INDUSTRIAL APPLICABILITY

[0105] The silk material of the present invention can be used for a purpose as a raw material of an outer skin coating product for human use such as outer skin preparations, non-medical skin agents and beauty products or as a medical material, for a purpose as a plant growth promoter, or for other purposes such as an absorbent, a filter material and an abrasive material. Further, this silk material has much possibility of utilization such as coating for material, dying of cloths.

Claims

1. A method of preparing a denatured silk material of various colors characterized in comprising heat-treating natural silk, half-degummed silk or degummed silk or a mixture thereof in an atmosphere of air flow under 0.5 to 1.5 atmospheres at a temperature of 150 to 500 °C for a certain period of time.
2. A method claimed in claim 1 characterized in that a heat-treatment period is in a range of several minutes to 20 hours.
3. A method of preparing a denatured silk material of various colors characterized in comprising heat-treating natural silk, half-degummed silk or degummed silk or a mixture thereof in an atmosphere of inert gas flow selected independently from nitrogen, helium, neon, argon, krypton and xenon or mixture thereof under 0.5 to 1.5 atmospheres

at a temperature of 150 to 500 °C for a certain period of time.

4. A method claimed in claim 3 characterized in that the heat-treatment period is in a range of several minutes to 20 hours.

5. A method claimed in any of claims 1 to 4 characterized in that natural silk, half-degummed silk, degummed silk or a mixture thereof is in the form of a film, powder, fiber, yarn, fabric, braid or mixture thereof.

6. A method claimed in claim 3 or 4 characterized in that various colors include black, yellow, brown, dark brown, red, purple, blue and gray or natural tints thereof.

7. A denatured silk material of various colors characterized in being obtained by heat-treating natural silk, half-degummed silk or degummed silk or a mixture thereof in an atmosphere of air flow under 0.5 to 1.5 atmospheres at a temperature of 150 to 500 °C for a certain period of time.

8. A denatured silk material claimed in claim 7 characterized in that a heat-treatment period is in a range of several minutes to 20 hours.

9. A denatured silk material of various colors characterized in being obtained by heat-treating natural silk, half-degummed silk or degummed silk or a mixture thereof in an atmosphere of inert gas flow selected independently from nitrogen, helium, neon, argon, krypton and xenon or mixture thereof under 0.5 to 1.5 atmospheres at a temperature of 150 to 500 °C for a certain period of time.

10. A denatured silk material claimed in claim 9 characterized in that the heat-treatment period is in a range of several minutes to 20 hours.

11. A denatured silk material claimed in any of claims 7 to 10 characterized in that the material is used for a purpose as an outer skin coating product for human use.

12. A denatured silk material claimed in claim 11 characterized in that the outer skin coating product for human use is a medical material for outer skin, non-medical material for outer skin or beauty products.

13. A denatured silk material claimed in any of claims 7 to 10 characterized in that the denatured silk material is used for a purpose as a medical material.

14. A denatured silk material claimed in any of claims 7 to 10 characterized in that the denatured silk material is used for a purpose as a plant growth promoter.

15. A denatured silk material claimed in any of claims 7 to 10 characterized in that the denatured silk material is used for a purpose as an absorbent or a filter material.

16. A denatured silk material claimed in any of claims 7 to 10 characterized in that the denatured silk material is used for a purpose as an abrasive material.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/05784

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl.⁴ D01C3/00, D01B7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl.⁴ D01C3/00, D01B7/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-1997
Kokai Jitsuyo Shinan Koho 1971-1997 Jitsuyo Shinan Toroku Koho 1996-1997

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 67517, C2 (Jun Takei, Tatsuzo Daiwa), 30 September, 1925 (30. 09. 25), Full text (Family: none)	1-16
A	JP, 48-7075, B1 (Takeshi Baba), 2 March, 1973 (02. 03. 73), Full text (Family: none)	1-16

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"A" document member of the same patent family

Date of the actual completion of the international search
9 February, 1999 (09. 02. 99)

Date of mailing of the international search report
16 February, 1999 (16. 02. 99)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)